Method Development for the Detection of Cyanide in Water by SPME-GC-MS

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HCN Detection Method Development

- Review method development principles
- Scientific method
- Parameters chosen for HCN detection

I. Investigation Procedures

1. Know or learn the particular field/specialty.
2. Ask the right question (i.e., what's important?).
3. Lit review- generally and specifically what's been done on this subject or around it before.
4. Select instrument, GC column, extraction method, GC-MS method, sampling matrix of interest.

I. Investigation Procedures (cont)

5. Optimize fiber if SPME (or use what's recommended in literature).
6. Optimize sampling temp, time, and LOD range. Do time and temperature uptake curves, One Way ANOVA w/ Tukey's post-hoc analysis to find best sampling time & temp.
7. Can do liquid injection calibration curve (how much is on my fiber, in my sample and recovered).
8. Trial your method in the lab- and preferably, in the field. Use common interferences.

II. Scientific Method

- Observe
- Question
- Form hypothesis
- Make prediction based on the hypothesis
- Test hypothesis (experiment)
- Analyze results
- Report results

III. HCN Detection Method Development

- U.S. Army Center for Environmental Health Research expressed an interest in method development for HCN in water to my research advisor, CDR Phil Smith. USACEHR provided the funding for this research.
- I took CDR Smith's preliminary method development for detection of KCN in water (which gives HCN in the water and headspace) and expanded it.
- The concentration of interest is based on the 1996 U.S. Tri-Service short term max exposure standard for drinking water (6 mg/L of free cyanide for 5L of water consumption/person/day). EPA max concentration level for drinking water= 0.2 ppm.

III. Lit Review

- SPME-GC-MS and SPME-GC-NPD previously used to detect HCN in blood [1-3].
- SPME-GC-MS used to detect HCN in air [4].
- Most lab and field detection methods for cyanide based on spectrophotometry, titration, or colorimetric test strips.
- KCN (oral LD_{50} 2 mg/kg), Ca_2CN, NaCN are common cyanide salts that disassociate in water. Cyanide poisoning by ingestion, inhalation, or dermal exposure very rapid, interferes with cell respiration process.

III. HCN Detection Method Development

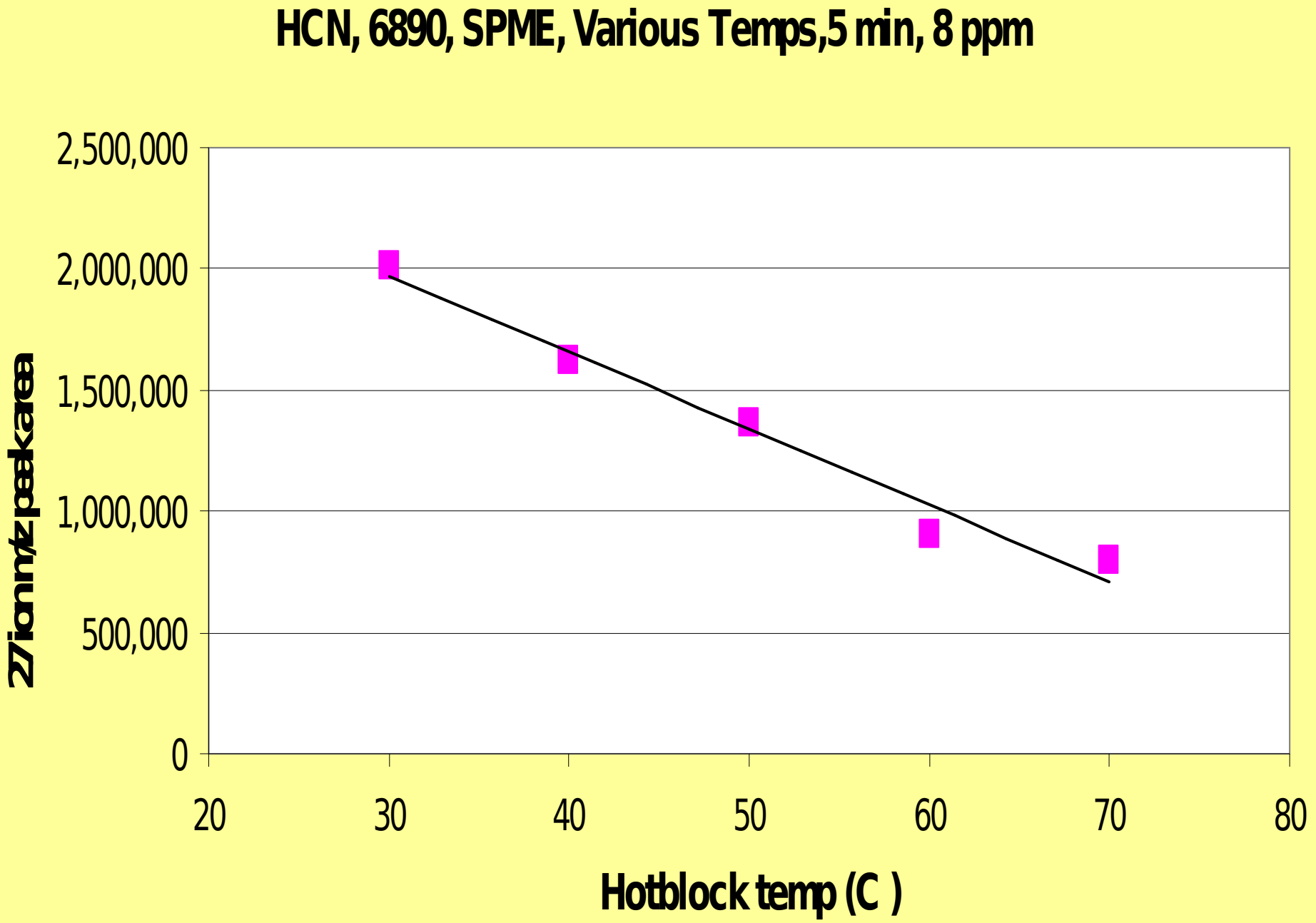
- Based on CDR Smith's prelim work, chose 85 μm Carboxen/Polydimethylsiloxane (CAR/PDMS) SPME fiber, 30 m x 0.32 mm I.D. GS-GasPro PLOT column, salting with Na_2SO_4, acidification with H_2SO_4, and 2 mL sample size in 20 mL crimp-topped vials.
- Benchtop GC-MS: Agilent 6890/5973 w/ LEAP CombiPAL autosampler. He 2.0 mL/min. Oven: 60 ˚C for 1.0 min, 25 ˚C/min to 175 ˚C, 35 ˚C/min to 260 ˚C, hold for 5.0 min.

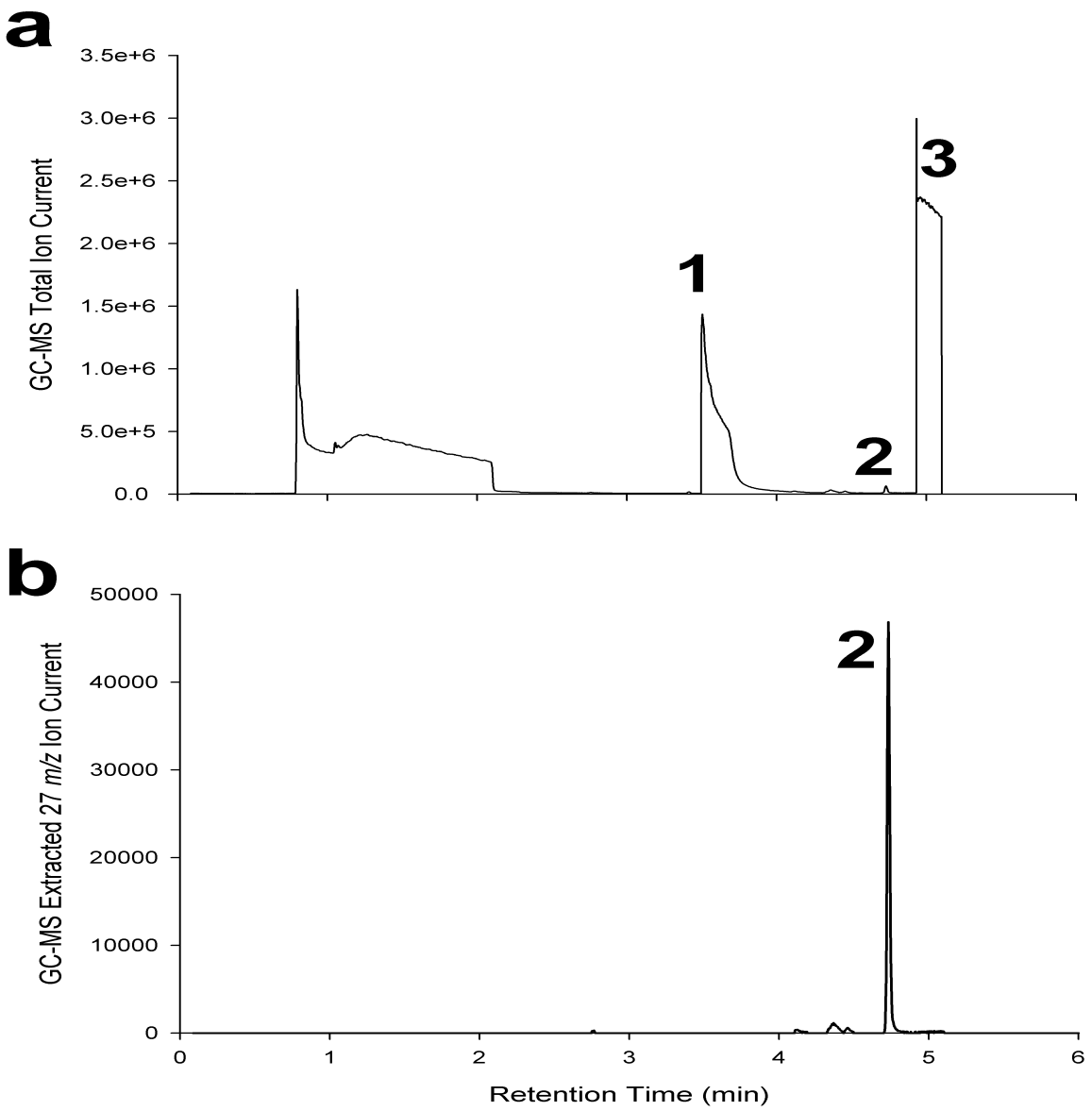
III. Method Development

- Selected optimum sampling temperature.
- Selected optimum sampling time.
- Explored acidification and salting
- Determined method sensitivity
- Used optimized method for cyanide in DI, pond, and tap water plus BTEX & MTBE.
- Export method to mobile GC-MS.

III. Methods: Sampling Temp

- Sampled for 5 min from 30 to 70 ˚C on 8.4 ppm CN^- samples (salted and acidified) after 5 min equilibration (stir and heat).
- 2.0 mL solution (serial dilution from stock solution) + 1.0 g Na_2SO_4 + 0.25 mL H_2SO_4.
- 30 ˚C statistically same as 40 ˚C but better than 50 ˚C and higher (comparison of extracted 27 ion m/z peak areas, 1-Way ANOVA + Tukey's Post Hoc Analysis).


HCN, 6890, SPME, Various Temps,5 min, 8 ppm
2,500,000
2,000,000
1,500,000
1,000,000
500,000
0
20
30
40
50
60
70
80
Hotblock temp (C)



1=sulfur dioxide

2= HCN

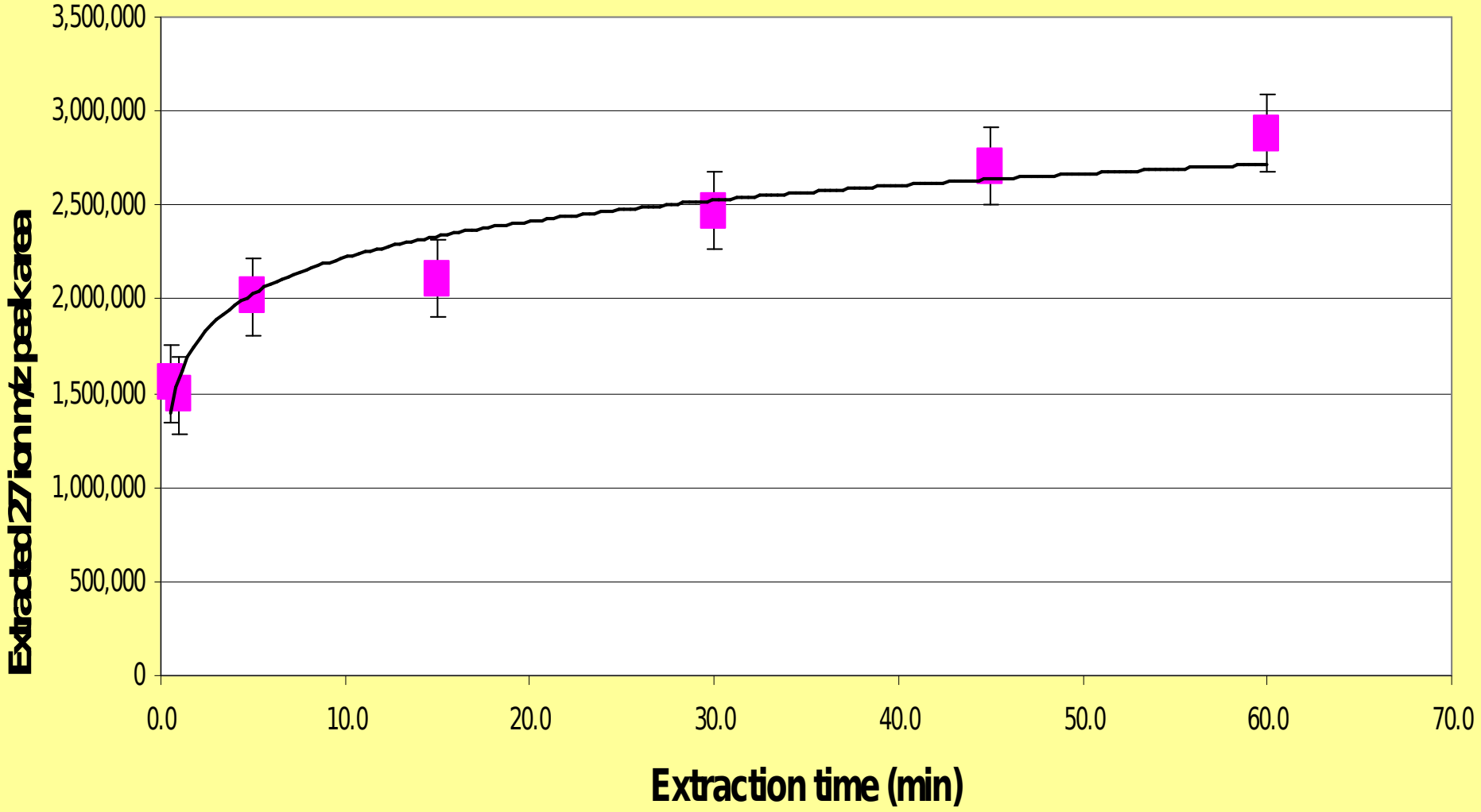
3= water

Fig 3a. SPME/GC-MS total ion chromatogram from analysis of 1.1 ppm aqueous CN^-, headspace SPME sampling, 5.0 min extraction,
with salt and acid added (CAR/PDMS, 30 ˚C). **Fig 3b.** SPME/GC-MS 27 *m/z* extracted ion chromatogram from analysis of 1.1 ppm
aqueous CN^-, headspace SPME sampling, 5.0 min extraction, with salt and acid added (CAR/PDMS, 30 ˚C).

III. Methods: Sampling Time

- Using optimized temperature, sampled 8.4 ppm CN^- samples for 0.5, 1, 5, 15, 30, 45, and 60 min. Approached equilibrium ~ 45 min, but 5 min gave adequate sensitivity and reproducibility and is better for field work (quicker).

HCN on 6890, SPME, 30C, Time Uptake



III. Methods: Acid and Salt Addition

- Went back and checked our assumption and prelim work that addition of acid and salt gave the best results.
- Comparison of extracted 27 *m/z* ion peak area showed use of acid + salt gave best results ($p=0.04$) compared to no acid, no salt, and no acid or salt samples.

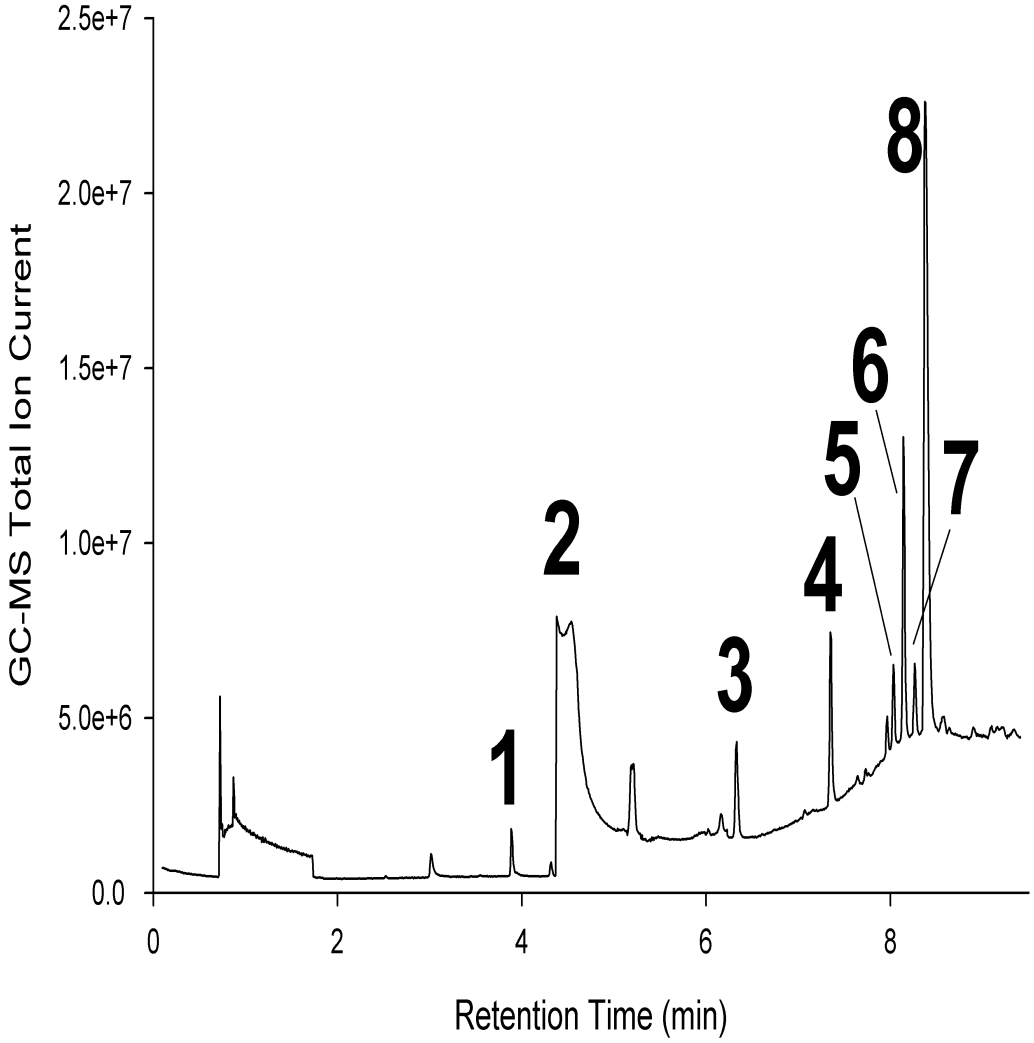
III. Method: Sensitivity

- Used 5 min extraction at 30 ˚C to determine sensitivity of method. Achieved reliable quantitation of CN^- down to 1.1 ppm and identification down to 0.3 ppm in DI water.
- Selected ion monitoring (SIM) scan with 26 and 27 *m/z* ion provided identification of cyanide down to 0.07 ppm in DI water.

III. Method Challenge and Export

- Successfully detected 8.4 ppm and 1.1 ppm CN^- in DI, pond, and tap water spiked with 10 ppm BTEX and MTBE on benchtop GC.

- Exported method to USMC CBIRF Mobile Van, 6890/5973 (no autosampler, H carrier gas). Successfully detected same levels and contaminants in field situation.



1= HCN
2= water
3= benzene
4= toluene
5= ethylbenzene
6=m-, p-xylenes
7= o-xylene
8= MTBE

Fig. 4. GC-MS chromatogram for 8.4 ppm aqueous CN^-, with 10 ppm BTEX and MTBE in tap water with salt a
headspace SPME sampling, analyzed using van-mounted GC-MS under field conditions, (CAR/PDMS, 30 ˚C, 5

Conclusions

- Method development for detection of a chemical in water by SPME-GC-MS is based on knowing the field, reviewing appropriate literature, making a hypothesis, testing the hypothesis in the lab and field, and reporting your results and findings.

QUESTIONS?

References

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2. A. Calafat, S Stanfill, J. Chromatogr. B, 772 (2002) 131.
3. K. Takekawa, M. Oya, A. Kido, O. Suzuki, Chromatographia 47 (1998) 209.
4. P.A. Smith, M.V. Sheely, T.A. Kluchinsky, Jr., J. Sep. Science 25 (2002) 917.